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<p>(54) Title: A METHOD OF WASHING FABRICS USING A DETERGENT COMPOSITION COMPRISING A TERPOLYMER</p> <p>(57) Abstract</p> <p>The present invention is directed to a method of washing fabrics, comprising using a laundry detergent composition comprising a detergent surfactant and a terpolymer; wherein the terpolymer comprises at least a first monomeric unit comprising a weak acid function, a second monomeric unit comprising a strong acid function, and a third monomeric unit comprising a nonionic function.</p>		

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A METHOD OF WASHING FABRICS USING A DETERGENT  
COMPOSITION COMPRISING A TERPOLYMER

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BACKGROUND

Detergent formulators are typically faced with the task of devising products to remove a broad spectrum of soils and stains from fabrics. Such soils and stains are caused by use of the fabric prior to washing. However, many fabrics when washed become stained due to the wash environment. For example, some fabrics, especially white cottons, begin to turn yellow after repeated washings. Consequently, detergent formulators are faced with an additional task of not only removing existing stains, but preventing further staining caused by the wash environment.

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Based on the foregoing, there is a need for a method of washing fabrics which inhibits the yellowing of fabrics caused by repeated washings, thereby maintaining the whiteness of the fabric.

SUMMARY

The present invention is directed to a method of washing fabrics, comprising using a laundry detergent composition comprising a deterative surfactant and a terpolymer; wherein the terpolymer comprises at least a first monomeric unit comprising a weak acid function, a second monomeric unit comprising a strong acid function, and a third monomeric unit comprising a nonionic function.

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Such a method satisfies the need for a method of washing fabrics which prevents the yellowing and/or maintains the whiteness of a fabric even after repeated washings.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure with the appended claims.

35

DETAILED DESCRIPTION

The following is a list of definitions for terms used herein.

"Alkyl" means a carbon-containing chain, preferably from about C<sub>1</sub> to about C<sub>10</sub>, more preferably from about C<sub>1</sub> to about C<sub>6</sub>, more preferably still from about C<sub>1</sub> to about C<sub>4</sub>; which may be straight, branched or cyclic; preferably straight or branched, more preferably straight; substituted (mono- or poly-) or unsubstituted; and saturated.

"Aalkyl" means R'-R'', wherein R' is an aryl and R'' is an alkyl.

"Aryl" means an aromatic; substituted (mono- or poly-) or unsubstituted, preferably unsubstituted. Preferred aryls are phenyl, puridyl, pyrimidyl and naphthyl; more preferred is phenyl.

"Comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

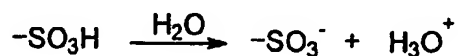
"Cycloalkyl" means a cyclic alkyl (*i.e.*, having one or more closed rings).

"Terpolymer" refers to a polymer formed from three or more monomers.

"HMI" means heavy metal ions, and for purposes of discussion herein, includes Fe<sup>+2</sup>, Fe<sup>+3</sup>, Mn<sup>+2</sup>, Mn<sup>+3</sup>, Mn<sup>+4</sup>, Cu<sup>+1</sup>, Cu<sup>+2</sup>, Zn<sup>+2</sup> and Pb<sup>+2</sup>; and their oxide and hydroxide salts.

"Nonionic functional monomer" refers to a monomer unit which doesn't have an ionic charge when placed in acidic, basic, or neutral solutions.

"Strong acid functional monomer" refers to a monomer unit having one or more functional groups which completely dissociate in water. For example:



"Weak acid functional monomer" refers to a monomer unit having one or more functional groups which only partially dissociate in water. For example:



All percentages are by weight of total composition unless specifically stated otherwise.

All ratios are weight ratios unless specifically stated otherwise.

All ppm (parts per million) references are the amounts in the final detergent composition, unless specifically stated otherwise.

All temperatures are in degrees Celsius (°C), unless specifically  
5 stated otherwise.

The present invention relates to a method of washing fabrics, comprising using a detergent composition comprising a deterative surfactant and a terpolymer; wherein the terpolymer comprises at least a first monomeric unit comprising a weak acid function, a second  
10 monomeric unit comprising a strong acid function, and a third monomeric unit comprising a nonionic function.

In studying why certain fabrics lose their whiteness (e.g., turn yellow) after several washings, we believe without intending to be bound by theory, we have identified the cause of this loss of whiteness  
15 as well as a solution to this previously unidentified cause. We have surprisingly discovered that fabrics exposed to wash or rinse water containing HMI have a significantly increased tendency to lose their whiteness and/or yellow over time. Again, without intending to be bound by theory, we believe it is caused by the HMI adhering to the  
20 fabric. However, we further discovered the surprising fact that yellowing typically occurs when HMI are present in the rinse water, rather than the wash water. As a result, it was necessary to identify a material which remains on the fabric (i.e., having an affinity for the fabric, hereinafter "fabric substantive") following the wash cycle, so it  
25 will be present to act during the rinse cycle. Unfortunately, many products tested failed to be fabric substantive, and consequently were not available to act on the HMI during the rinse cycle. It is known that the pH is typically lower in the rinse as compared to the wash. Without intending to be bound by theory, we believe this drop in pH alters  
30 and/or decreases fabric substantivity. We discovered the terpolymers used in the compositions of the present invention to be surprisingly fabric substantive during the wash and rinse cycles, despite the drop in pH from wash to rinse. Consequently, these terpolymers have been found to be surprisingly efficacious in the maintenance of whiteness

and/or prevention of yellowing of fabrics washed/rinsed in water containing HMI.

The aspects and embodiments of the present invention set forth in this document have many surprising advantages, including  
5 maintaining the whiteness and/or preventing the yellowing of fabrics even after repeated washings. Without intending to be bound by theory, it is believed the terpolymer used in the present invention chelates the HMI in the wash and/or rinse water. Chelation is achieved when the polymer and/or chelant binds with the HMI through ion-ion  
10 interaction, the resulting complex remaining soluble in the water solution. It is also believed the terpolymer disperses HMI by "wrapping" itself around the HMI salts (e.g.,  $\text{Fe}(\text{OH})_3$ ), thereby preventing the insoluble HMI salts from adhering to the fabric.

An additional benefit which may be conferred by the  
15 compositions used in the method of the present invention is the prevention of the decomposition of bleach by HMI in the wash. A common problem found in detergent compositions comprising bleach is the decomposition of the bleach by HMI in the wash and/or rinse water. Consequently, chelants are added to detergent compositions  
20 comprising bleach to prevent such HMI from decomposing the bleach. The use of the terpolymers in the compositions of the present invention may additionally prevent or reduce bleach decomposition due to the chelant effects of the terpolymer. Consequently, this may reduce or eliminate the need to add additional "bleach protecting" chelants to the  
25 detergent composition.

Another possible benefit of the method of the present invention is the prevention of incrustation caused by, e.g., carbonates, silicate and/or orthophosphates, normally found in detergent compositions. In hard water, such carbonates form, e.g., calcium carbonate which,  
30 when deposited in fabric, may bestow a harsh or rough feeling to the fabric. The terpolymers used in the compositions of the present invention may prevent the deposition of such calcium carbonate by dispersing the calcium carbonate.

A further possible benefit of the composition used in the method  
35 of the present invention is improved physical properties. For example,

if the form of the detergent composition is a granular detergent, the terpolymer bestows an additional benefit in which the composition has improved free flowing properties. Such free flowing properties, in turn, improve processability during the manufacture and packaging of the detergent composition. Previously known detergent compositions (*i.e.*, those not containing the terpolymers of the present invention) can run into difficulties during processing including, clumping, caking or sticking of the detergent granules, which may result in the clogging of processing lines. However, the terpolymers used in the compositions of the present invention have a powder form. Consequently, the terpolymer facilitates the free flow of the overall detergent composition through the processing line by preventing or reducing the frequency of clumping, caking or sticking of the detergent granules.

The laundry detergent composition used in the method of the present invention may be in any suitable form, for example, high density liquids, light liquids or other pourable forms, granules, laundry bars, gels, or pastes. The terpolymers of the present invention can be formulated into any deterative matrix chosen by the formulator.

The present invention is described in more detail as follows.

#### 20 Terpolymer

The terpolymers used in the detergent compositions comprise a first monomeric unit, a second monomeric unit, and a third monomeric unit. Optionally, other monomer units, in addition to these three, may make up the terpolymer, so long as these additional monomers do not significantly interfere with the whitening maintenance and/or prevention of yellowing properties bestowed by the first, second and third monomeric units.

Preferably, the detergent composition comprises at least about 0.2% of the terpolymer.

Preferably the terpolymer has a molecular weight of from about 500 to about 36,000 Daltons; more preferably from about 1,000 to about 20,000 Daltons; more preferably still, from about 3,000 to about 6,000 Daltons.

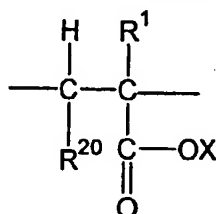
Preferably the ratio of first monomeric unit to second monomeric unit to third monomeric unit in the terpolymer is from about 3:2:1 to

about 8:6:5, more preferably from about 4:3:3 to about 8:1:1, more preferably still from about 5:3:2 to about 6:2:2.

Examples of terpolymers useful in the present invention as well as synthesis of such terpolymers include those set forth in U.S. Patent  
 5 4,711,725, issued December 8, 1987.

a. First Monomeric Unit

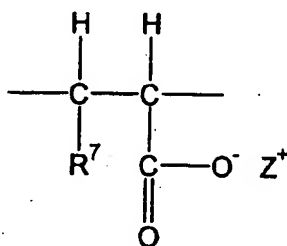
The first monomeric unit comprises a weak acid function. Preferably the first monomeric unit comprises a carboxylate function. More preferably, the first monomeric unit has the following structure



10

$\text{R}^1$  is H or  $\text{CH}_3$ , preferably H.  $\text{R}^{20}$  is H or  $\text{C(O)-OX}$ . X is independently H, a metal cation or  $\text{N-(R}^2)_4$  wherein  $\text{R}^2$  is H, a  $\text{C}_1\text{-C}_4$  hydroxyalkyl, or mixtures thereof; preferably X is H or  $\text{Na}^+$ ; more preferably X is  $\text{Na}^+$ .

15 More preferably, the first monomeric unit has the following structure

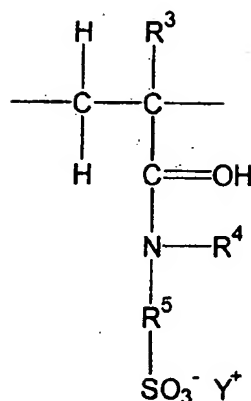


$\text{R}^7$  is independently H or  $\text{-COO}^- \text{Z}^+$ ; preferably H.  $\text{Z}^+$  is independently H or Na, preferably Na (i.e.,  $\text{-COO}^- \text{Na}^+$ ).

20 b. Second Monomeric Unit

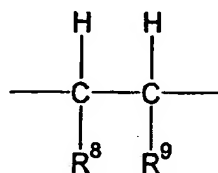
The second monomeric unit comprises a strong acid function. Preferably the second monomeric unit comprises a sulfonate function. More preferably the second monomeric unit has the following structure



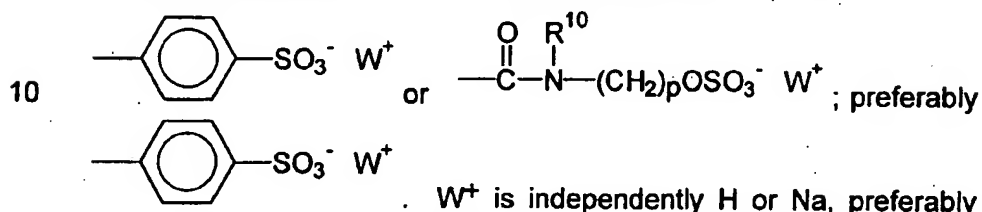


- $\text{R}^3$  is H or  $\text{CH}_3$ ; preferably H.  $\text{R}^4$  is H or  $\text{C}_1\text{-C}_4$  alkyl; preferably H or  $\text{CH}_3$ ; more preferably  $\text{CH}_3$ .  $\text{R}^5$  is  $\text{C}_1\text{-C}_8$  alkyl or  $\text{C}_1\text{-C}_8$  aralkyl; preferably  $\text{C}_1\text{-C}_4$ ; more preferably  $\text{C}_1$ ; more preferably still alkyl. Y is H, a metal cation or  $\text{N-(R}^{21})_4$ ; preferably H or  $\text{Na}^+$ ; more preferably  $\text{Na}^+$ .  $\text{R}^{21}$  is H, a  $\text{C}_1\text{-C}_4$  hydroxyalkyl, or mixtures thereof.

Preferably the second monomeric unit has the structure



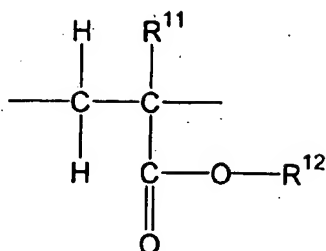
$\text{R}^8$  is independently H or  $\text{-COOH}^- \text{Na}^+$ ; preferably H.  $\text{R}^9$  is



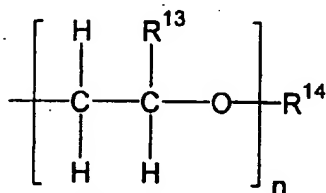
15 c. Third Monomeric Unit

The third monomeric unit comprises a nonionic function. Preferably the third monomeric unit is a vinyl ester, vinyl acetate or substituted acrylamide; more preferably methyl substituted acrylamides.

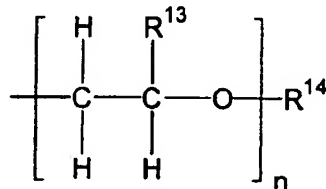
20 Preferably the vinyl ester has the structure



R<sup>11</sup> is H or CH<sub>3</sub>; preferably H. R<sup>12</sup> is a C<sub>1</sub>-C<sub>6</sub> alkyl, a C<sub>6</sub>-C<sub>10</sub> aryl, a C<sub>6</sub>-C<sub>10</sub> aralkyl, or

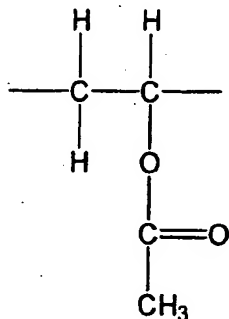


5 ;preferably C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>6</sub> aryl or

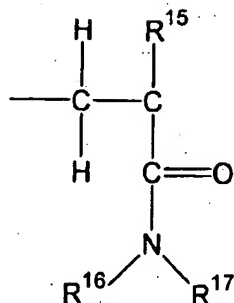


;more preferably C<sub>1</sub>-C<sub>4</sub> alkyl. R<sup>13</sup> is H or CH<sub>3</sub>; preferably H. R<sup>14</sup> is H or a C<sub>1</sub>-C<sub>6</sub> alkyl; preferably H. n is an integer of from 1 to about 3; preferably 1.

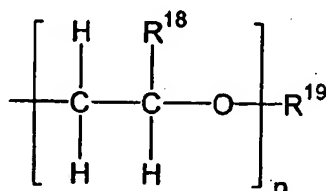
10 Preferably, the vinyl acetate has the structure



Preferably the substituted acrylamide has the structure

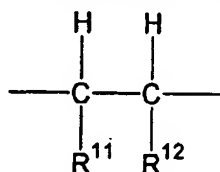


R<sup>15</sup> is H or CH<sub>3</sub>; preferably H. R<sup>16</sup> and R<sup>17</sup> are independently H, a C<sub>1</sub>-C<sub>8</sub> alkyl, a C<sub>6</sub>-C<sub>8</sub> cycloalkyl, a benzyl, or



5 as defined above, such that R<sup>18</sup> and R<sup>19</sup> are not both H.

More preferably, the third monomeric unit has the structure



R<sup>11</sup> is independently H, -COO<sup>-</sup> H<sup>+</sup>, or -COO<sup>-</sup> Na<sup>+</sup>; preferably H. R<sup>12</sup>

is:  $-(\text{CH}_2)_q\text{CH}_3$ ,  $-(\text{CH}_2)_q\text{OH}$ ,  $-\overset{\text{O}}{\parallel}\text{C}-\text{O}(\text{CH}_2)_q\text{CH}_3$ , or

10  $-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{N}(\text{R}^{13})\text{R}^{14}$ ; preferably  $-(\text{CH}_2)_q\text{OH}$ ,  $-\overset{\text{O}}{\parallel}\text{C}-\text{O}(\text{CH}_2)_q\text{CH}_3$ , or

$-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{N}(\text{R}^{13})\text{R}^{14}$ ; more preferably  $-(\text{CH}_2)_q\text{OH}$  or

$-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{N}(\text{R}^{13})\text{R}^{14}$ ; more preferably still  $-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{N}(\text{R}^{13})\text{R}^{14}$ .

q is independently from 0 to 6; preferably from about 0 to about 3; more preferably 1. R<sup>13</sup> and R<sup>14</sup> are independently  $-(\text{CH}_2)_m\text{CH}_3$

or H. m is from 0 to about 6; preferably from about 0 to about 3; more preferably 0.

Deterstive Surfactant

5 The detergent composition also comprises a deterstive surfactant. Preferably the detergent composition comprises at least about 0.01% of a deterstive surfactant; more preferably at least about 0.1%; more preferably at least about 1%; more preferably still, from about 1% to about 55%.

10 Preferred deterstive surfactants are cationic, anionic, nonionic, ampholytic, zwitterionic, and mixtures thereof, further described herein below. Nonlimiting examples of deterstive surfactants useful in the detergent composition include, the conventional C<sub>11</sub>-C<sub>18</sub> alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C<sub>10</sub>-C<sub>20</sub> alkyl sulfates ("AS"), the C<sub>10</sub>-C<sub>18</sub> secondary (2,3) alkyl  
15 sulfates of the formula CH<sub>3</sub>(CH<sub>2</sub>)<sub>x</sub>(CHOSO<sub>3</sub><sup>-</sup>M<sup>+</sup>) CH<sub>3</sub> and CH<sub>3</sub>(CH<sub>2</sub>)<sub>y</sub>(CHOSO<sub>3</sub><sup>-</sup>M<sup>+</sup>) CH<sub>2</sub>CH<sub>3</sub> where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy sulfates ("AE<sub>x</sub>S"; especially EO 1-7 ethoxy  
20 sulfates), C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C<sub>10</sub>-18 glycerol ethers, the C<sub>10</sub>-C<sub>18</sub> alkyl polyglycosides and their corresponding sulfated polyglycosides, and C<sub>12</sub>-C<sub>18</sub> alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the  
25 C<sub>12</sub>-C<sub>18</sub> alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C<sub>6</sub>-C<sub>12</sub> alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C<sub>12</sub>-C<sub>18</sub> betaines and sulfobetaines ("sultaines"), C<sub>10</sub>-C<sub>18</sub> amine oxides, and the like, can also be included in the overall compositions. The C<sub>10</sub>-C<sub>18</sub> N-alkyl  
30 polyhydroxy fatty acid amides can also be used. Typical examples include the C<sub>12</sub>-C<sub>18</sub> N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C<sub>10</sub>-C<sub>18</sub> N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C<sub>12</sub>-C<sub>18</sub> glucamides can be used for low  
35 sudsing. C<sub>10</sub>-C<sub>20</sub> conventional soaps may also be used. If high

sudsing is desired, the branched-chain C<sub>10</sub>-C<sub>16</sub> soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

Additional Detergent Composition Components

5       The detergent compositions herein may optionally comprise other known detergent cleaning components including alkoxyated polycarboxylates, bleaching compounds, brighteners, chelating agents, clay soil removal / anti-redeposition agents, dye transfer inhibiting agents, enzymes, enzyme stabilizing systems, fabric softeners, 10 polymeric soil release agents, polymeric dispersing agents, suds suppressors. The detergent composition may also comprise other ingredients including carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions.

15   a.   Alkoxyated Polycarboxylates

Alkoxyated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 *et seq.* Chemically, these materials comprise 20 polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula  $-(CH_2CH_2O)_m(CH_2)_nCH_3$  wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 25 2000 to about 50,000. Such alkoxyated polycarboxylates can comprise from about 0.05% to about 10% of the compositions herein.

b.   Bleaching Compounds - Bleaching Agents and Bleach Activators

30       The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach 35 activators will typically be from about 0.1% to about 60%, more

typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard  
5 surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

Another category of bleaching agent that can be used without  
10 restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in  
15 U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-  
20 oxoperoxyacaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

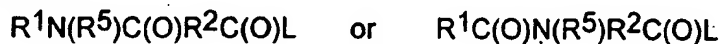
Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium  
25 pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to  
30 about 1,000 micrometers, not more than about 10% of said particles being smaller than about 200 micrometers and not more than about 10% of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various  
35 commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (*i.e.*, during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

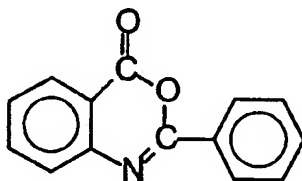
Highly preferred amido-derived bleach activators are those of the formulae:



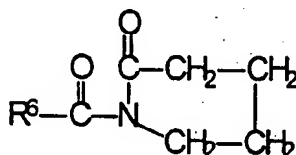
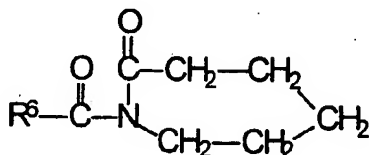
wherein  $R^1$  is an alkyl group containing from about 6 to about 12 carbon atoms,  $R^2$  is an alkylene containing from 1 to about 6 carbon atoms,  $R^5$  is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamido-caproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



5 wherein R<sup>6</sup> is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl  
10 caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, which discloses acyl caprolactams,  
15 including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines, or silicon. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these



catalysts include  $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$ ,  $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$ ,  $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_4$ ,  $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$ ,  $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})\text{-(OCH}_3)_3(\text{PF}_6)$ , and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

c. Brightener

Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.05% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic

White CWD, available from Hilton-Davis, located in Italy; the 2-(4-stryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis- (1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(stryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino  
5 coumarin; 1,2-bis(-venzimidazol-2-yl)ethylene; 1,3-diphenyl-phrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-stryl-naphth-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho- [1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton. Anionic brighteners are preferred herein.

10 d. Builders

Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal  
15 of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Liquid formulations typically comprise from about 5% to about 50%, more  
20 typically about 5% to about 30%, by weight, of detergent builder. Granular formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

25 Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including  
30 bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation  
35 that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- $\text{Na}_2\text{SiO}_5$  morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula  $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$  wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- $\text{Na}_2\text{SiO}_5$  (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

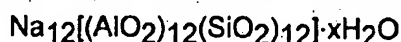
Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in

structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-

trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxy-  
5 disuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their  
10 availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C<sub>5</sub>-C<sub>20</sub> alkyl and alkenyl succinic acids and salts thereof. A particularly  
20 preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent  
25 Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C<sub>12</sub>-C<sub>18</sub> monocarboxylic acids, can also be  
30 incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by  
35 the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium ortho-phosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

e. Chelating Agents

The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in

acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as  
5 described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites,  
10 layered silicates and the like.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

15 f. Clay Soil Removal / Anti-redeposition Agents

The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Granular detergent compositions which contain these compounds typically contain from about 0.01% to about  
20 10.0% by weight of the water-soluble ethoxylates amines; liquid detergent compositions typically contain about 0.01% to about 5%.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued  
25 July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in  
30 European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti redeposition agents known in  
35 the art can also be utilized in the compositions herein. Another type of

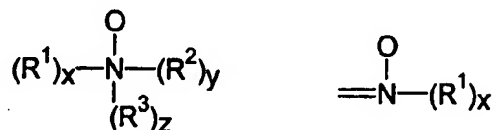
preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

g. Dye Transfer Inhibiting Agents

The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers suitable for use herein contain units having the following structural formula:  $R-A_x-P$ ; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures:  $-NC(O)-$ ,  $-C(O)O-$ ,  $-S-$ ,  $-O-$ ,  $-N=$ ; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein  $R^1$ ,  $R^2$ ,  $R^3$  are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a  $pK_a < 10$ , preferably  $pK_a < 7$ , more preferred  $pK_a < 6$ .



Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

The most preferred polyamine N-oxide useful as dye transfer inhibiting polymers in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also suitable for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization".) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention also may employ as a dye transfer inhibitor a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to

about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696. Compositions containing PVP dye transfer inhibitors can also contain polyethylene glycol ("PEG") having an average molecular weight from  
5 about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

h. Enzymes

10 Enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from substrates, for the prevention of refugee dye transfer in fabric laundering, and for fabric restoration. Suitable enzymes include proteases, amylases,  
15 lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal  
20 enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

"Detergent enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry, hard surface cleaning or personal care detergent composition.  
25 Preferred detergent enzymes are hydrolases such as proteases, amylases and lipases. Preferred enzymes for laundry purposes include, but are not limited to, proteases, cellulases, lipases and peroxidases. Highly preferred for automatic dishwashing are amylases and/or proteases, including both current commercially available types  
30 and improved types which, though more and more bleach compatible though successive improvements, have a remaining degree of bleach deactivation susceptibility.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-  
35 effective amount". The term "cleaning effective amount" refers to any

amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics, dishware and the like. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. For certain detergents, such as in automatic dishwashing, it may be desirable to increase the active enzyme content of the commercial preparation in order to minimize the total amount of non-catalytically active materials and thereby improve spotting/filming or other end-results. Higher active levels may also be desirable in highly concentrated detergent formulations.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to

Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

In more detail, an especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in the patent applications of A. Baeck, et al, entitled "Protease-Containing Cleaning Compositions" having US Serial No. 08/322,676, and C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, both filed October 13, 1994.

Amylases suitable herein, especially for, but not limited to automatic dishwashing purposes, include, for example, -amylases described in GB 1,296,839 to Novo; RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo. FUNGAMYL® from Novo is especially useful. Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp. 6518-6521. Certain preferred embodiments of the present compositions can make use of amylases having improved stability in detergents such as automatic dishwashing types, especially improved oxidative stability as measured against a reference-point of TERMAMYL® in commercial use in 1993. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide / tetraacetylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, measured versus the above-identified reference-point amylase.

Stability can be measured using any of the art-disclosed technical tests. See, for example, references disclosed in WO 9402597. Stability-enhanced amylases can be obtained from Novo or from Genencor International. One class of highly preferred amylases herein

5 have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus* - amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Oxidative stability-enhanced amylases vs. the above-identified reference amylase are preferred for use,

10 especially in bleaching, more preferably oxygen bleaching, as distinct from chlorine bleaching, detergent compositions herein. Such preferred amylases include (a) an amylase according to the hereinbefore referenced WO 9402597, Novo, Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine,

15 preferably threonine, of the methionine residue located in position 197 of the *B. licheniformis* alpha-amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens*, *B. subtilis*, or *B. stearothermophilus*; (b) stability-enhanced amylases as described by Genencor International in a paper

20 entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B*

25 *licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was

30 measured in CASCADE® and SUNLIGHT®; (c) particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL®. Other particularly preferred oxidative stability enhanced amylase include

35 those described in WO 9418314 to Genencor International and WO

9402597 to Novo. Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See  
5 WO 9509909 A to Novo.

Other amylase enzymes include those described in WO 95/26397 and in co-pending application by Novo Nordisk PCT/DK96/00056. Specific amylase enzymes for use in the detergent compositions of the present invention include -amylases characterized  
10 by having a specific activity at least 25% higher than the specific activity of Termamyl at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas -amylase activity assay. (Such Phadebas -amylase activity assay is described at pages 9-10, WO 95/26397.) Also included herein are -amylases  
15 which are at least 80% homologous with the amino acid sequences shown in the SEQ ID listings in the references. These enzymes are preferably incorporated into laundry detergent compositions at a level from 0.00018% to 0.060% pure enzyme by weight of the total composition, more preferably from 0.00024% to 0.048% pure enzyme  
20 by weight of the total composition.

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307, Barbesgoard et al, March 6, 1984, discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase  
25 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® and CELLUZYME® (Novo) are especially useful. See  
30 also WO 9117243 to Novo.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open  
35 Feb. 24, 1978. This lipase is available from Amano Pharmaceutical

Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," or "Amano-P." Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan;  
5 *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase and amylase variants stabilized against  
10 peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 and RD 94359044.

In spite of the large number of publications on lipase enzymes, only the lipase derived from *Humicola lanuginosa* and produced in *Aspergillus oryzae* as host has so far found widespread application as  
15 additive for fabric washing products. It is available from Novo Nordisk under the tradename Lipolase™, as noted above. In order to optimize the stain removal performance of Lipolase, Novo Nordisk have made a number of variants. As described in WO 92/05249, the D96L variant of the native *Humicola lanuginosa* lipase improves the lard stain removal  
20 efficiency by a factor 4.4 over the wild-type lipase (enzymes compared in an amount ranging from 0.075 to 2.5 mg protein per liter). Research Disclosure No. 35944 published on March 10, 1994, by Novo Nordisk discloses that the lipase variant (D96L) may be added in an amount corresponding to 0.001-100- mg (5-500,000 LU/liter) lipase variant per  
25 liter of wash liquor. The present invention provides the benefit of improved whiteness maintenance on fabrics using low levels of D96L variant in detergent compositions containing the AQA surfactants in the manner disclosed herein, especially when the D96L is used at levels in the range of about 50 LU to about 8500 LU per liter of wash solution.

30 Cutinase enzymes suitable for use herein are described in WO 8809367 A to Genencor.

Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for  
35 "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present.

in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromoperoxidase. Peroxidase-containing detergent compositions are disclosed in WO 89099813 A, October 19, 1989 to Novo and WO 8909813 A to Novo.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

i. Enzyme Stabilizing Agent

Enzyme-containing, including but not limited to, liquid compositions, herein may comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the deterative enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.



One stabilizing approach is the use of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. Calcium ions are generally more effective than magnesium ions and are preferred herein if only one type of cation is being used. Typical detergent compositions, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 8 to about 12 millimoles of calcium ion per liter of finished detergent composition, though variation is possible depending on factors including the multiplicity, type and levels of enzymes incorporated. Preferably water-soluble calcium or magnesium salts are employed, including for example calcium chloride, calcium hydroxide, calcium formate, calcium malate, calcium maleate, calcium hydroxide and calcium acetate; more generally, calcium sulfate or magnesium salts corresponding to the exemplified calcium salts may be used. Further increased levels of Calcium and/or Magnesium may of course be useful, for example for promoting the grease-cutting action of certain types of surfactant.

Another stabilizing approach is by use of borate species. See Severson, U.S. 4,537,706. Borate stabilizers, when used, may be at levels of up to 10% or more of the composition though more typically, levels of up to about 3% by weight of boric acid or other borate compounds such as borax or orthoborate are suitable for liquid detergent use. Substituted boric acids such as phenylboronic acid, butaneboronic acid, p-bromophenylboronic acid or the like can be used in place of boric acid and reduced levels of total boron in detergent compositions may be possible though the use of such substituted boron derivatives.

Stabilizing systems of certain cleaning compositions, for example automatic dishwashing compositions, may further comprise from 0 to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of

water that comes in contact with the enzyme, for example during dish- or fabric-washing, can be relatively large; accordingly, enzyme stability to chlorine in-use is sometimes problematic. Since perborate or percarbonate, which have the ability to react with chlorine bleach, may  
5 present in certain of the instant compositions in amounts accounted for separately from the stabilizing system, the use of additional stabilizers against chlorine, may, most generally, not be essential, though improved results may be obtainable from their use. Suitable chlorine scavenger anions are widely known and readily available, and, if used,  
10 can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Likewise, special enzyme  
15 inhibition systems can be incorporated such that different enzymes have maximum compatibility. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate,  
20 acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired. In general, since the chlorine scavenger function can be performed by ingredients separately listed under better recognized functions, (e.g., hydrogen peroxide sources), there is no absolute requirement to add a separate  
25 chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any enzyme scavenger or stabilizer which is  
30 majorly incompatible, as formulated, with other reactive ingredients, if used. In relation to the use of ammonium salts, such salts can be simply admixed with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that  
35 described in US 4,652,392, Baginski et al.

j. Fabric Softeners

Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December 13, 1977, as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416, Crisp et al, March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued September 22, 1981.

k. Polymeric Soil Release Agent

Known polymeric soil release agents, hereinafter "SRA", can optionally be employed in the present detergent compositions. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the compositions.

Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles, thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the SRA to be more easily cleaned in later washing procedures.

SRA's can include a variety of charged, e.g., anionic or even cationic species, see U.S. 4,956,447, issued September 11, 1990 to Gosselink, et al., as well as noncharged monomer units, and their structures may be linear, branched or even star-shaped. They may include capping moieties which are especially effective in controlling molecular weight or altering the physical or surface-active properties. Structures and charge distributions may be tailored for application to different fiber or textile types and for varied detergent or detergent additive products.

Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a

titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without, of course, forming a densely crosslinked overall structure.

- 5        Suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the backbone, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Such ester oligomers can be prepared by: (a) ethoxylating allyl alcohol; (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure; and (c) reacting the product of (b) with sodium metabisulfite in water. Other
- 10        SRA's include the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al., for example those produced by transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Other examples of SRA's
- 15        include: the partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, methyl (Me)-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al., the latter
- 20        being typical of SRA's useful in both laundry and fabric conditioning products, an example being an ester composition made from m-sulfobenzoic acid monosodium salt, PG and DMT, optionally but preferably further comprising added PEG, e.g., PEG 3400.
- 25        SRA's also include: simple copolymeric blocks of ethylene
- 30        terephthalate or propylene terephthalate with polyethylene oxide or
- 35

35        terephthalate or propylene terephthalate with polyethylene oxide or

polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; the C<sub>1</sub>-C<sub>4</sub> alkyl celluloses and C<sub>4</sub> hydroxyalkyl  
5 celluloses, see U.S. 4,000,093, December 28, 1976 to Nicol, et al.; and the methyl cellulose ethers having an average degree of substitution (methyl) per anhydroglucose unit from about 1.6 to about 2.3 and a solution viscosity of from about 80 to about 120 centipoise measured at 20°C as a 2% aqueous solution. Such materials are  
10 available as METOLOSE SM100 and METOLOSE SM200, which are the trade names of methyl cellulose ethers manufactured by Shin-etsu Kagaku Kogyo KK.

Suitable SRA's characterized by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C<sub>1</sub>-C<sub>6</sub>  
15 vinyl esters, preferably poly(vinyl acetate), grafted onto polyalkylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available examples include SOKALAN SRA's such as SOKALAN HP-22, available from BASF, Germany. Other SRA's are polyesters with  
20 repeat units containing 10-15% by weight of ethylene terephthalate together with 80-90% by weight of polyoxyethylene terephthalate derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Commercial examples include ZELCON 5126 from DuPont and MILEASE T from ICI.

25 Another preferred SRA is an oligomer having empirical formula (CAP)<sub>2</sub>(EG/PG)<sub>5</sub>(T)<sub>5</sub>(SIP)<sub>1</sub> which comprises terephthaloyl (T), sulfoisophthaloyl (SIP), oxyethyleneoxy and oxy-1,2-propylene (EG/PG) units and which is preferably terminated with end-caps (CAP), preferably modified isethionates, as in an oligomer comprising one  
30 sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a defined ratio, preferably about 0.5:1 to about 10:1, and two end-cap units derived from sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said SRA preferably further comprises from 0.5% to 20%, by weight of the oligomer, of a  
35 crystallinity-reducing stabilizer, for example an anionic surfactant such

as linear sodium dodecylbenzenesulfonate or a member selected from xylene-, cumene-, and toluene- sulfonates or mixtures thereof, these stabilizers or modifiers being introduced into the synthesis vessel, all as taught in U.S. 5,415,807, Gosselink, Pan, Kellett and Hall, issued  
 5 May 16, 1995. Suitable monomers for the above SRA include Na-2-(2-hydroxyethoxy)-ethanesulfonate, DMT, Na-dimethyl-5-sulfoisophthalate, EG and PG.

Yet another group of preferred SRA's are oligomeric esters comprising: (1) a backbone comprising (a) at least one unit selected  
 10 from the group consisting of dihydroxysulfonates, polyhydroxy sulfonates, a unit which is at least trifunctional whereby ester linkages are formed resulting in a branched oligomer backbone, and combinations thereof; (b) at least one unit which is a terephthaloyl moiety; and (c) at least one unsulfonated unit which is a 1,2-  
 15 oxyalkyleneoxy moiety; and (2) one or more capping units selected from nonionic capping units, anionic capping units such as alkoxylated, preferably ethoxylated, isethionates, alkoxylated propanesulfonates, alkoxylated propanedisulfonates, alkoxylated phenolsulfonates, sulfoaroyl derivatives and mixtures thereof. Preferred are esters of the  
 20 empirical formula:



wherein CAP, EG/PG, PEG, T and SIP are as defined hereinabove, (DEG) represents di(oxyethylene)oxy units, (SEG) represents units derived from the sulfoethyl ether of glycerin and related moiety units,  
 25 (B) represents branching units which are at least trifunctional whereby ester linkages are formed resulting in a branched oligomer backbone, x is from about 1 to about 12, y' is from about 0.5 to about 25, y'' is from 0 to about 12, y''' is from 0 to about 10, y'+y''+y''' totals from about 0.5 to about 25, z is from about 1.5 to about 25, z' is from 0 to about  
 30 12; z + z' totals from about 1.5 to about 25, q is from about 0.05 to about 12; m is from about 0.01 to about 10, and x, y', y'', y''', z, z', q and m represent the average number of moles of the corresponding units per mole of said ester and said ester has a molecular weight ranging from about 500 to about 5,000.

Preferred SEG and CAP monomers for the above esters include Na-2-(2-,3-dihydroxypropoxy)ethanesulfonate ("SEG"), Na-2-{2-(2-hydroxyethoxy) ethoxy} ethanesulfonate ("SE3") and its homologs and mixtures thereof and the products of ethoxylating and sulfonating allyl alcohol. Preferred SRA esters in this class include the product of transesterifying and oligomerizing sodium 2-{2-(2-hydroxyethoxy)ethoxy}ethanesulfonate and/or sodium 2-[2-{2-(2-hydroxyethoxy)ethoxy}ethoxy]ethanesulfonate, DMT, sodium 2-(2,3-dihydroxypropoxy) ethane sulfonate, EG, and PG using an appropriate Ti(IV) catalyst and can be designated as (CAP)2(T)5(EG/PG)1.4(SEG)2.5(B)0.13 wherein CAP is (Na+O<sub>3</sub>S[CH<sub>2</sub>CH<sub>2</sub>O]3.5)- and B is a unit from glycerin and the mole ratio EG/PG is about 1.7:1 as measured by conventional gas chromatography after complete hydrolysis.

Additional classes of SRA's include: (I) nonionic terephthalates using diisocyanate coupling agents to link polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al.; and (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal hydroxyl groups to trimellitate esters. With the proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.. Other classes include: (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violland et al.; (IV) poly(vinyl caprolactam) and related co-polymers with monomers such as vinyl pyrrolidone and/or dimethylaminoethyl methacrylate, including both nonionic and cationic polymers, see U.S. 4,579,681, Ruppert et al.; (V) graft copolymers, in addition to the SOKALAN types from BASF, made by grafting acrylic monomers onto sulfonated polyesters. These SRA's assertedly have soil release and anti-redeposition activity similar to known cellulose ethers: see EP 279,134 A, 1988, to Rhone-Poulenc Chemie. Still other classes

include: (VI) grafts of vinyl monomers such as acrylic acid and vinyl acetate onto proteins such as caseins, see EP 457,205 A to BASF (1991); and (VII) polyester-polyamide SRA's prepared by condensing adipic acid, caprolactam, and polyethylene glycol, especially for treating polyamide fabrics, see Bevan et al., DE 2,335,044 to Unilever N. V., 1974. Other useful SRA's are described in U.S. Patents 4,240,918, 4,787,989 and 4,525,524.

I. Polymeric Dispersing Agent

Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble



salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

m. Suds Suppressors

Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C<sub>18</sub>-C<sub>40</sub> ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 50°C, and a minimum boiling point not less than about 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting

point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

- (i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1,500 cs. at 25°C;
- (ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of  $(\text{CH}_3)_3\text{SiO}_{1/2}$  units of

- SiO<sub>2</sub> units in a ratio of from (CH<sub>3</sub>)<sub>3</sub> SiO<sub>1/2</sub> units and to SiO<sub>2</sub> units of from about 0.6:1 to about 1.2:1; and
- (iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel.

- 5 In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.
- 10 To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from about 0.001 to about 1, preferably from about 0.01 to about 0.7, most preferably from about 0.05 to about 0.5, weight % of said silicone suds suppressor, which comprises (1) a nonaqueous emulsion of a primary
- 15 antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a
- 20 copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than about 2 weight %; and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Patents 4,978,471, Starch, issued December 18, 1990, and 4,983,316, Starch, issued January 8,
- 25 1991, 5,288,431, Huber et al., issued February 22, 1994, and U.S. Patents 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

- The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene
- 30 glycol/polypropylene glycol, all having an average molecular weight of less than about 1,000, preferably between about 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight %, preferably more than about 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than about 1,000, more preferably between about 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between about 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like PLURONIC L101.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C<sub>6</sub>-C<sub>16</sub> alkyl alcohols having a C<sub>1</sub>-C<sub>16</sub> chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount. By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0% to about 5% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to about 5%, by weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically

utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling  
5 sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds  
10 suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished  
15 compositions.

n. Other Ingredients

A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or  
20 pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C<sub>10</sub>-C<sub>16</sub> alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C<sub>10</sub>-C<sub>14</sub> monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such  
25 suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as MgCl<sub>2</sub>, MgSO<sub>4</sub>, and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

30 Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the  
35 porous substrate. In use, the deterative ingredient is released from the

substrate into the aqueous washing liquor, where it performs its intended deterative function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a  
5 proteolytic enzyme solution containing 3%-5% of C<sub>13-15</sub> ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of  
10 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

15 Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6  
20 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

The detergent compositions herein will preferably be formulated  
25 such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and about 11, preferably between about 7.5 and 10.5. Liquid dishwashing product formulations preferably have a pH between about 6.8 and about 9.0. Laundry products are typically at pH 9-11. Techniques for controlling pH at  
30 recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

#### Examples

The following examples further describe and demonstrate the preferred embodiments within the scope of the present invention. The  
35 examples are given solely for the purpose of illustration, and are not to

be construed as limitations of the present invention since many variations thereof are possible without departing from its spirit and scope.

#### Example 1

- 5 This example shows a granule detergent composition useful in the method of the present invention.

	<u>Component</u>	<u>% by weight of composition</u>
	NaCFAS (C <sub>12</sub> -C <sub>18</sub> ) (coconut fatty alcohol sulfate)	21
10	A(C <sub>12</sub> -C <sub>14</sub> ) E6.5 (akyl ethoxylate)	4
	STPP (sodium tripolyphosphate)	17.5
	Na Carbonate	20.0
	Zeolite	8.0
	Nonanoyl Benzene Sulfonate	2.3
15	Na Perborate	2.28
	Zn phthalocynine sulfonate	0.3
	ACUMER 3100 (terpolymer)	2.25
	Diethylenetriamine pentaphosphonate (Na salt)	1
	Protease Enzyme (protease activity at 1.0 AU/g)	0.25
20	Amylase Enzyme (amylase activity at 60,000 AMU/g)	0.50
	Lipase Enzyme (lipase activity at 100,000 LU/g)	0.12
	Cellulase Enzyme (cellulase activity at 5,000 CEVU/g)	0.15
	Water (including water of hydration), sodium sulfate and other minor ingredients)	balance

25

#### Example 2

This example shows a liquid detergent composition useful in the method of the present invention.

	<u>Component</u>	<u>% by weight of composition</u>
30	NaC <sub>25</sub> -AS	20.5
	A(C <sub>12</sub> -14)E3S	5.0
	A(C <sub>12</sub> -13)E6.5	4.5
	C <sub>12</sub> -14 Fatty Acid	5.0
	Citric Acid	3.0
35	Ethyl Alcohol	5.5



	Hexane-Diol	8.5
	Boric Acid	3.5
	ACUMER 5000 (terpolymer)	3.0
	Protease Enzyme (protease activity at 1.0 AU/g)	1.5
5	Lipase Enzyme (lipase activity at 100,000 LU/g)	0.2
	Cellulase Enzyme (cellulase activity at 5,000 CEVU/g)	0.1
	Fluorescent Whitening Agent 49 (4,4' distilbene)	0.1
	Water (including water of hydration) and other minor ingredients)	balance

10

Example 3

This example shows a bar detergent composition useful in the method of the present invention.

	<u>Component</u>	<u>% by weight of composition</u>
15	NaLAS (C <sub>12-18</sub> )	22.5
	NaAS	3
	Na <sub>2</sub> CO <sub>3</sub>	3
	Diethylenetriamine pentaphosphonate (Na salt)	0.70
	Polyethylene Oxide (MW=600)	0.30
20	Bentonite Clay	10
	Sokolan CP-5 (acrylic maleic copolymer, MW=36,000)	0.7
	ACUMER 5000 (terpolymer)	1.5
	TSPP (trisodium tripolyphosphate)	5
	STPP	5
25	Zeolite	1.25
	Protease Enzyme (protease activity at 1.0 AU/g)	0.10
	Amylase Enzyme (amylase activity at 60,000 AMU/g)	0.75
	Lipase Enzyme (lipase activity at 100,000 LU/g)	0.1
	Cellulase Enzyme (cellulase activity at 5,000 CEVU/g)	0.15
30	Water (including water of hydration), sodium sulfate and other minor ingredients)	balance

Example 4

This example shows a method for machine washing fabric using the composition of Example 1.

White clothes are sorted and washed separately from colored clothes. 40g of the composition of Example 1 is place in the automatic washing machine. White clothes having a total weight of approximately 1.5kg are then added to the washer. After turning on  
5 the washer, the washer adds approximately 33 liters of water. The washer is allowed to continue through its automatic cycle of approximately a 10 minute wash followed by two batch rinses. The clothes are then allowed to air, sun or machine dry. The washed clothes have no yellowing and the white clothes retain their whiteness.

10

Example 5

This example shows a method for hand washing fabric using the composition of Example 1.

Approximately 10 liters of water is placed in a basin. 40g of the composition of Example 1 is dissolved in the water. The white clothes  
15 (approximately 1.5 kg) are washed separately from the colored clothes. The clothes are scrubbed between the hands or by scrubbing them against a wash board. The clothes are occasionally dipped into the wash solution during scrubbing. After all the clothes have been washed, the wash solutions is discarded and replaced with fresh clean  
20 water for rinsing. Rinsing is done by swirling and scrubbing the clothes together between the hands and squeezing the water out of the clothes. The rinse water is replaced with fresh clean rinse water. Rinsing and replacement of rinse water continues until the last rinse water is clean and without visible and persistent suds. After rinsing,  
25 the clothes are either air, sun or machine dried. The washed clothes have no yellowing and the white clothes retain their whiteness.

Example 6

This example shows a method for cleaning fabric using the composition of Example 2.

30 White clothes are pre-rinsed to remove any particulate soils in a basin containing approximately 20 liters of water. The pre-rinse water is discarded and replaced with fresh clean water. The clothes are washed one by one by directly applying the bar into the fabric and then scrubbing between the hands, or by using a scrubbing implement such  
35 as a scrubbing board. When all the clothes are washed, the wash

- water is discarded and replaced with fresh clean water. The clothes are then batch rinsed until there is no visible sign of suds or until the last rinse water is clear. After rinsing, the clothes are either air, sun or machine dried. The clothes are then allowed to machine dry or air dry.
- 5 The washed clothes have no yellowing and the white clothes retain their whiteness.

#### Example 7

This example shows a method for cleaning fabric using the composition of Example 3.

- 10 White clothes are washed separately from the colored clothes. Stains and soils that are concentrated in a particular area are pretreated with a small amount of the composition of Example 3. The clothes (approximately 1.5 kg) are then placed in an automatic washing machine. 39.6 g of the composition of Example 3 is further
- 15 added to the clothes in the machine. After turning on the washer, the washer adds approximately 33 liters of water. The washer is allowed to continue through its automatic cycle of approximately a 10 minute wash followed by two 3-min rinses). After rinsing, the clothes are either air, sun or machine dried. The clothes are then allowed to
- 20 machine dry or air dry. The washed clothes have no yellowing and the white clothes retain their whiteness.

All publications, patent applications, and issued patents mentioned hereinabove are hereby incorporated in their entirety by reference.

- 25 It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art and are to be included in the spirit and purview of this application and scope of the appended claims.

30

35

## WHAT IS CLAIMED IS:

1. A method of washing fabrics, comprising using a laundry detergent composition comprising:

a) at least about 0.01% of a deterative surfactant; and

b) at least about 0.2% of a terpolymer, wherein the terpolymer comprises:

i) from about 30 to about 80% of a first monomeric unit comprising a weak acid function;

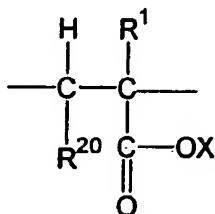
ii) from about 20 to about 60% of a second monomeric unit comprising a strong acid function; and

iii) from about 10 to about 50% of a third monomeric unit comprising a nonionic function.

2. The method of Claim 1, wherein the first monomeric unit has a carboxylate function and the second monomeric unit has a sulfonate function.

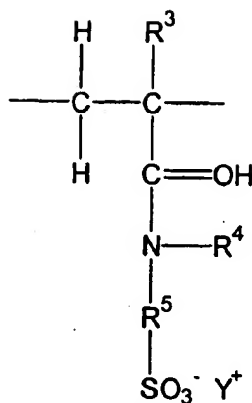
3. The method of Claim 2, wherein

a) the first monomeric unit has the structure



wherein  $\text{R}^1$  is H or  $\text{CH}_3$ ;  $\text{R}^{20}$  is H or  $\text{C}(\text{O})-\text{OX}$ ; and X is independently H, a metal cation or  $\text{N}(\text{R}^2)_4$  wherein  $\text{R}^2$  is H, a  $\text{C}_1$ - $\text{C}_4$  hydroxyalkyl, or mixtures thereof;

b) the second monomeric unit has the structure



wherein  $\text{R}^3$  is H or  $\text{CH}_3$ ;  $\text{R}^4$  is H or  $\text{C}_1\text{-C}_4$  alkyl; and  $\text{R}^5$  is  $\text{C}_1\text{-C}_8$  alkyl or  $\text{C}_1\text{-C}_8$  aralkyl; and Y is H, a metal cation or  $\text{N}(\text{R}^{21})_4$  wherein  $\text{R}^{21}$  is H, a  $\text{C}_1\text{-C}_4$  hydroxyalkyl, or mixtures thereof; and

- c) the third monomeric unit is a vinyl ester, vinyl acetate or substituted acrylamide.

4. The method of Claim 3, wherein  $\text{R}^{20}$  is H and the composition further comprises a builder.

5. The method of Claim 4, wherein the composition comprises from about 0.5% to about 10% of the terpolymer.

6. The method of Claim 5, wherein the terpolymer is formed from three different monomers.

7. The method of Claim 6, wherein the composition comprises from about 1% to about 5% of the terpolymer.

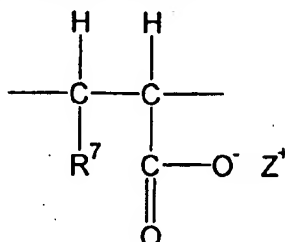
8. The method of Claim 7, wherein the deterative surfactant is an anionic surfactant, nonionic surfactant, zwitterionic surfactant, anionic surfactant, ampholytic surfactant, or mixtures thereof.

9. A method of washing fabrics, comprising using a laundry detergent composition comprising:

- a) at least about 0.1% of a deterative surfactant, wherein the deterative surfactant is an anionic surfactant, nonionic surfactant, zwitterionic surfactant, anionic surfactant, ampholytic surfactant, or mixtures thereof;

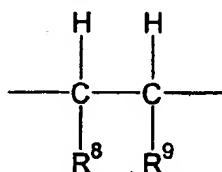
10 b) from about 0.5% to about 10% of a terpolymer, wherein the terpolymer comprises

i) from about 30 to about 80% of a first monomer unit having the structure

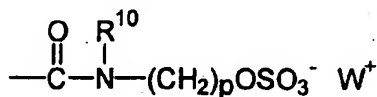
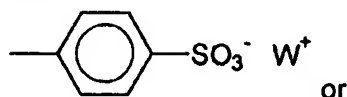


15 wherein  $\text{R}^7$  is independently H, or  $\text{---COO}^- \text{Z}^+$ ; wherein  $\text{Z}^+$  is independently H or Na;

ii) from about 20 to about 60% of a second monomer unit having the structure

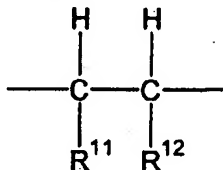


20 wherein  $\text{R}^8$  is independently H,  $\text{---COO}^- \text{W}^+$ ; and  $\text{R}^9$  is

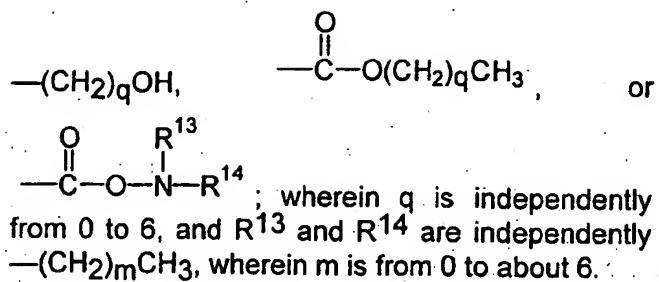


25 wherein p is from 1 to about 6; and  $\text{R}^{10}$  is  $\text{CH}_3$ ; and wherein  $\text{W}^+$  is H or Na.

iii) from about 10 to about 50% of a third monomer unit having the structure



30 wherein  $\text{R}^{11}$  is independently H,  $\text{---COO}^- \text{H}^+$ , or  $\text{---COO}^- \text{Na}^+$ ; and  $\text{R}^{12}$  is  $\text{---}(\text{CH}_2)_q \text{CH}_3$ ,



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10. The method of Claim 9, wherein the composition comprises from about 1% to about 5% of the terpolymer, and further comprises a builder.

## INTERNATIONAL SEARCH REPORT

 Int. Application No  
 PCT/US 96/16652

 A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 6 C11D3/37

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 36 43 334 A (LION CORP) 9 July 1987 see essay nr. 4,7 see claims; tables I-III ---	1-10
A	US 4 711 725 A (AMICK DAVID R ET AL) 8 December 1987 cited in the application see claims 1-7 ---	1-3,9
A	EP 0 727 448 A (NAT STARCH CHEM INVEST) 21 August 1996 see page 7, line 52 - line 53; claims 1-4,21-25; example 2; tables 1,3,8 ---	1,2
A	DE 43 43 993 A (STOCKHAUSEN CHEM FAB GMBH) 29 June 1995 see claims 1,5-9,16; example 12 ---	1,2
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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- "P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

15 May 1997

Date of mailing of the international search report

20.06.97

Name and mailing address of the ISA

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Loiselet-Taisne, S



# INTERNATIONAL SEARCH REPORT

In International Application No

PCT/US 96/16652

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 584 709 A (HOECHST AG) 2 March 1994 see page 6, line 39 - line 46 see page 6, line 23 - line 24 see claims 1-3,7-9 -----	1

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information on patent family members

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